Magnetic Resonance Imaging, Vol. 16, Nos. 5/6, pp. 629–630, 1998

Printed in the USA.
0730-725X/98 $19.00 + .00

ELSEVIER

PII S0730-725X(98)00038-1

● *Short Communication*

CRYSTALLISATION OF CRYSTALLIZABLE AND AMORPHOUS POLYMER MIXTURES AND PECULIARITIES OF THEIR STRUCTURE: AN NMR STUDY

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After isothermal crystallization of the crystallizable poly(ethylene oxide)/amorphous poly(propylene oxide) mixture, partially crystalline structures were formed. They present a specific heterogeneous medium with a hard frame composed of the crystal phase. The isothermal crystallization of the mixture and molecular self-diffusion processes in the amorphous phase of the crystallized mixture was studied by nuclear magnetic resonance relaxation and nuclear magnetic resonance (NMR) with pulsed field gradient. The temporal dependencies of the apparent self-diffusion coefficient were analyzed and the heterogeneity sizes were estimated. The dependence of the heterogeneity size on the crystallization temperature can be qualitatively described by parameter δ, which includes the linear growth rate of the crystal and diffusion coefficient of the amorphous (more mobile) component. © 1998 Elsevier Science Inc.

Keywords: **NMR; Polymer crystallization; Self-diffusion; Porous structure.**

INTRODUCTION

Some of the partially crystalline polymers can be described as heterogeneous media with restricted translation motion of the molecules in the amorphous phase.[1] Thus a new aspect of the study of heterogeneous media appears. Usually, during discussion of the molecular diffusion in porous media of natural origin (formed under sedimentation or crystallization), assumptions about the influence of the external conditions on the formed structure are made. However, the experimental verification of these assumptions is rather complicated. In the course of the investigation of crystallization in partially crystalline polymer mixtures we have a unique chance to estimate the influence of the external conditions on the formed structure.

An influence of the crystallization rate and mobility of the components on the partially crystalline polymer morphology were described in the works of Keith and Padden[2] on the basis of a model of the growth of dendrite-type structures. The characteristic parameter of the structure is $\delta = D_a/a$, where D_a is the diffusion coefficient of the amorphous (more mobile) component and a is the linear growth rate. It is the purpose of this work to test this conception.

The samples studied were mixtures of crystallizable poly(ethylene oxide) with M = 20000, $M_w/M_n = 1.1$ ("Shuchardt") and noncrystallizable poly(propylene oxide) with M = 425 ("Ferak-Berlin"). The method of studying crystallization kinetics by nuclear magnetic resonance (NMR) relaxation was described earlier.[3,4] The analysis, based on the kinetic theory[5] of polymer crystallization, shows that the crystallization regime, surface free energies of the crystallites and mechanism of polymer chain folding remain unchanged for all crystallization temperatures and compositions. The linear growth rate was estimated as $a = (v^c)^{1/3}$, where v^c is the rate of the overall crystallization.

The pulsed field gradient experiment was performed using NMR apparatus with a maximum value for the field gradient amplitude of 50 T/m. The parameter δ is given by $\delta = D_{PPO}/a$, where D_{PPO} is the poly(propylene oxide) self-diffusion coefficient in the melt of the mixture.

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